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(54) Process for the removal of CO₂
and, if present H₂S from a gas mixture

(57) A process for removal of CO₂ and,
if present H₂S, from a gas mixture, in
which

- a) the gas mixture is contacted at
elevated pressure countercurrently
with a solvent comprising a tertiary
amine and a physical absorbent;
- b) the loaded solvent obtained is
flushed to a pressure higher than
the total partial pressure of CO₂ and
H₂S present in the loaded solvent at
the prevailing temperature;
- c) the loaded solvent obtained in step
b) is flashed to a pressure below the
total partial pressure of CO₂ and
H₂S present in the loaded solvent at
the prevailing temperature,
and semi-lean solvent obtained in step
c) is, optionally after all or part thereof
has been totally regenerated, used as
solvent in step a).

GB 2 103 645 A

SPECIFICATION

Process for the removal of CO₂ and, if present, H₂S from a gas mixture

5 The invention relates to a process for removal of CO₂ and, if present, H₂S from a gas mixture.

In many cases it is necessary to remove CO₂ and, if present, H₂S and other sulphur-containing impurities such as COS from gas mixtures. The removal of H₂S and/or other sulphur-containing impurities from gas mixtures may be necessary in order to render these gas mixtures suitable for catalytic conversions using sulphur-sensitive catalysts, or to reduce environmental pollution if the said gas mixtures or combustion gases obtained therefrom are discharged to the atmosphere.

Examples of CO₂-containing gas mixtures from which H₂S and/or other sulphur-containing compounds generally have to be removed are gases obtained by partial combustion, or complete or partial gasification, of oil and coal, refinery gases, town gas, natural gas, coke-oven gas, water gas, propane and propene.

25 Removal of CO₂ from gas mixtures, either as such from a gas mixture which contains no or virtually no H₂S (e.g. natural gases), or in admixture with H₂S in case the latter compound is present in the gas mixture, is often necessary to bring the gas mixtures on a desired calorific value and/or to avoid corrosion in transport lines and/or to avoid freezing in cryogenic equipment and/or to avoid transport of CO₂ which is of no value in the gas mixture ultimately to be used for a certain purpose.

35 In many cases the CO₂ and, if present the H₂S, will be removed from the said gas mixtures using liquid solvents, which will often be basic. At least part of the CO₂ present in the gas mixtures will be absorbed in the liquid solvent together with at least part of the H₂S, if present. The H₂S and CO₂ (which in this specification are also indicated as acid gases) will be removed from the said gas mixtures at the pressure of the gas mixture concerned, i.e. in many cases at elevated pressure.

45 The loaded solvent obtained after absorption of CO₂ and, if present, H₂S from the gas mixture is to be regenerated partly or totally, during which regeneration H₂S, if present, and CO₂ are set free.

In case H₂S is present in an appreciable content in the gas obtained after regeneration of the loaded solvent, this gas cannot be discharged to the atmosphere before at least most of the H₂S has been removed therefrom. The H₂S is very suitably removed from this gas by converting it to elemental sulphur, which is separated off. The conversion of H₂S into elemental sulphur is generally carried out in the art by means of a Claus process in which some of the H₂S is oxidized to SO₂, and sulphur and water are formed by reaction of H₂S with SO₂, with or without the assistance of a suitable catalyst. In order to be able to carry out a Claus process, the molar percentage of H₂S in a mixture with CO₂ must be at least about 15. If this percentage is between about 15 and

H₂S therein to SO₂, and subsequently mixing the resultant SO₂-containing gas with the balance of the H₂S-containing gas, after which the Claus reaction can be further carried out at elevated temperature and preferably in the presence of a catalyst. In case the gas contains about 40% mol H₂S or more, the Claus process can be carried out by combusting the gas with a quantity of air which is sufficient to convert one-third part of the H₂S into SO₂, and subsequently reacting the H₂S and SO₂ to form sulphur and water.

In many instances the gas set free during regeneration of the loaded solvent is unsuitable for use in a Claus process, the H₂S content thereof being too low and further processes for increasing the H₂S content are to be carried out with such a gas.

In case the gas set free during regeneration should have an H₂S content which is sufficiently high for use in a Claus process it may nevertheless be of importance to increase the H₂S content thereof, because in the latter case the total amount of gas to be used in the Claus process is lower, and accordingly the installation can be of smaller size.

The increase in H₂S content of the gas set free during regeneration of the loaded solvent can, of course, be achieved by preferential absorption of the H₂S from that gas in a suitable solvent, and regeneration of that solvent after loading. However, such a second absorption process is unattractive in view of the extra installations to be built and the extra amount of energy needed for regeneration of that loaded solvent.

The invention provides a process for the removal of CO₂ and, if present, H₂S from a gas mixture, in which process the energy needed for the regeneration of the solvent loaded with CO₂ and, if present, H₂S is very low, and in which process gases with high H₂S contents suitable to be used in a Claus process are obtained with a single absorption step from gas mixtures containing H₂S.

Accordingly, the invention provides a process for removal of CO₂ and, if present, H₂S from a gas mixture, which process is characterized in that:

- a) the gas mixture is contacted at elevated pressure countercurrently with a solvent which comprises a tertiary amine and a physical absorbent;
- b) the loaded solvent obtained is flashed at least once by pressure release to a pressure which is above the total partial pressure of the CO₂ and H₂S present in the loaded solvent at the prevailing temperature;
- c) the loaded solvent obtained in step b) is flashed at least once by pressure release to a pressure which is below the total partial pressure of the CO₂ and H₂S present in the loaded solvent at the prevailing temperature, and semi-lean solvent obtained in step c) is, optionally after all or part thereof has been totally regenerated, used as solvent in step a).

The solvent comprises a tertiary amine, a physical absorbent and preferably water.

Acid gases are able to react with tertiary amines. Very suitable tertiary amines are aliphatic, in particu-

tripropanolamine, triisopropanolamine, ethyldiethanolamine, dimethylethanolamine, diethylethanolamine. Preference is given to methyldiethanolamine.

A physical absorbent is a compound in which acid gases are soluble, but without undergoing a reaction therewith. Very suitable physical absorbents are sulfolane and substituted sulfolanes, alcohols with 1-5 carbon atoms per molecule (e.g. methanol), tetraethylene glycol dimethyl ether, N-methylpyrrolidone, alkylated carboxylic acid amides (e.g. dimethylformamide). Preference is given to sulfolane. The word "sulfolane" denotes the compound "tetrahydrothiophene 1,1-dioxide".

The contents of tertiary amine and physical absorbent (and, if present, water) in the solvent may vary between wide limits. Very suitably the solvent contains in the range of from 10 to 60% of tertiary amine, preferably methyldiethanolamine, in the range of from 15 to 55%w of physical absorbent, preferably sulfolane, and in the range of from 5 to 35%w of water.

It is essential that the solvent used in the process according to the invention comprises a tertiary amine and a physical absorbent. In modified processes solely differing from the process according to the invention in that the solvent contains a secondary and/or a primary amine instead of a tertiary amine or contains a tertiary amine but no physical absorbent, less CO₂ is set free in the flashing in step c), and accordingly, in case H₂S was present in the original gas mixture, the semi-lean solvent obtained in the partial regeneration in step c) contains H₂S and CO₂ in a lower molar ratio than obtained with the process according to the invention. Moreover, total regeneration (which in general is carried out by stripping with steam) of the said semi-lean solvent requires in the case of the above modified processes more steam and yields a mixture of CO₂ and H₂S in a less favourable molar ratio for a Claus process than in the case of the process according to the invention.

A modified process differing from that according to the invention in that the solvent comprises one or more physical absorbents only, amines being absent, requires in many cases more solvent and more absorption trays in an absorption column used in step a) to achieve the same amount of acid gases absorbed than the process according to the invention. Moreover, more non-acid gases are absorbed in solvents which comprise one or more physical absorbents only than in the solvents used in the process according to the invention, which non-acid gases are set free during the flashing in step b). In case a solvent is used which comprises one or more physical absorbents only, this amount of non-acid gases is so great that it is not attractive to use it as fuel (as can be done with the non-acid gases set free in step b) in the process according to the invention, and accordingly these non-acid gases need repressurizing (with the aid of capital intensive compressors) prior to recycling to step a).

The contacting of the gas mixture with the solvent in step a) is carried out at elevated pressure, which is considered to be a pressure of at least 5, in particular at least 10 bar. Preferably, the pressure is from 20 to

The contacting of the gas mixture with the solvent is very suitably carried out in a contacting zone, e.g. an absorption column which comprises in the range of from 15 to 80 contacting layers, such as valve trays, bubble cap trays, baffles and the like. It has surprisingly been found that by using the solvent in the process according to the invention the H₂S can substantially be removed from the gas mixture used as feed while regulating the amount of CO₂ which is left in the purified gas. This regulation can be achieved by regulating the solvent circulation, i.e. the ratio of solvent fed to the extracting zone and the amount of gas mixture fed thereto. In case no or hardly no H₂S is present in the gas mixture, the amount of CO₂ removed therefrom can also be regulated by the solvent circulation. If desired, the CO₂ can be removed to a very great extent. The solvent circulation can still be further reduced, if desired, by removing loaded solvent at an intermediate point from the contacting zone at the lower part thereof, externally cooling the removed loaded solvent, and reintroducing it to the lower part of the contacting zone for further contacting of the gas mixture to be purified, e.g. as described in British patent specification 1,589,231.

The temperature during the contacting of the gas mixture and the solvent in step a) may vary between wide limits. Temperatures in the range of from 15 to 110°C are very suitable, temperatures in the range of from 20 to 80°C are preferred.

In step a) all or the greater part of COS, if present, is removed from the gas mixture.

The loaded solvent obtained from step a) contains CO₂, H₂S (if any) and, in general, amounts of dissolved non-acid components from the gas mixture to be purified, e.g. hydrocarbons and/or hydrogen and/or carbon monoxide. These non-acid gases are to be removed at least partially from the loaded solvent by flashing in step b) to a pressure which is higher than the total partial pressure of the acid gases present in the loaded solvent. In this way only very small amounts of acid gases are released from the solvent together with the non-acid gases, e.g. hydrocarbons and/or hydrogen and/or carbon monoxide. If desired, the gas mixture obtained from the flashing in step b) may be recirculated to step a), but in order to avoid recompressing this gas mixture is preferably used for any other purpose, e.g. as fuel gas (if desired after removal of all or part of the H₂S present, e.g. by contacting the said gas mixture with a small amount of lean solvent). Non-acid gases have to be removed from the loaded solvent before this solvent is flashed to a pressure which is lower than the total partial pressure of the acid gases, because otherwise the hydrocarbons and/or hydrogen and/or carbon monoxide would be set free together with an appreciable amount of acid gases. As in many cases these acid gases or combustion gases obtained therefrom are to be discharged to the atmosphere, the hydrocarbons and/or hydrogen and/or carbon monoxide would be discharged or burnt simultaneously, which would be a waste of these valuable compounds.

Although the loaded solvent may be flashed in

in most cases the greater part of dissolved non-acid components will be removed in one flash step, and for that reason it is preferred to flash the loaded solvent once in step b).

- 5 The loaded solvent obtained in step b) - which besides acid gases contains only small amounts of other dissolved compounds - is flashed in step c) to a pressure below the total partial pressure of the acid gases in the said loaded solvent at the prevailing temperature. It has been found that in the process according to the invention (in which a solvent comprising a tertiary amine and a physical absorbent is used) the amount of CO₂ set free is much higher than in modified processes differing solely from the process according to the invention in that the solvent contains a secondary and/or primary amine instead of a tertiary amine or contains a tertiary amine, but no physical absorbent. In case the loaded solvent also contains H₂S the gas set free after the pressure release in step c) has a much higher molar ratio of CO₂ to H₂S than the molar ratio of these gases originally present in the loaded solvent. It is of advantage to heat the loaded solvent, e.g. to a temperature in the range of from 45 to 110°C before or during flashing in step c), because in that case the molar ratio of CO₂ to H₂S in the gases set free after the pressure release is still further increased. The above modified process in which a solvent is used which comprises a secondary or primary amine and a physical absorbent or a solvent which comprises a tertiary amine and no physical absorbent, gives a much lower molar ratio of CO₂ to H₂S in the gas set free after the pressure release. Because the gas set free in step c) has a higher molar ratio of CO₂ to H₂S than that of the original loaded solvent, the molar ratio of H₂S to CO₂ present in the solvent remaining after the pressure release in step c) is higher than originally.

Because at each pressure release in step c) the molar ratio of H₂S to CO₂ in the remaining solvent is increased, it may be of advantage to flash the loaded solvent in step c) at least twice, each time to a lower pressure or at a higher temperature in case the original gas mixture contains H₂S. In general, the pressure of the loaded solvent after the pressure release in step c) will be about atmospheric.

- In step c) a large amount of CO₂ is set free, and accordingly the loaded solvent is in fact regenerated to an appreciable extent, yielding semi-lean solvent. In case the original gas mixture was substantially free from H₂S the semi-lean solvent obtained in step c) contains CO₂ as the only acid gas, and it is preferentially used as such at least partially as solvent in step a); in many cases the amount of CO₂ present in the semi-lean solvent obtained in step c) will be so low that it is preferred to use this semi-lean solvent as the only solvent in step a). If desired, part or all of the semi-lean solvent obtained in step c) can be totally regenerated (e.g. by stripping with steam) and used as solvent in step a). In case totally regenerated solvent and semi-lean solvent are both used as solvents in step a) the former is preferentially introduced into the contacting zone at a point

In case the original gas mixture did not only contain CO₂ but also H₂S the acid gases set free during the flashing in step c) in a number of cases will contain so small amounts of H₂S that they can be discharged to the atmosphere after incineration. If desired or needed the H₂S present in the gases set free during the flashing in step c) may be removed therefrom by contacting these gases with a solvent under conditions which favour preferential removal of H₂S over CO₂. For such removal, e.g. a mixture comprising an amine and optionally a physical absorbent, may suitably be used, in particular the solvent to be used according to the present invention. In order to achieve a high selectivity for H₂S removal the contacting is very suitably carried out in a column with less than 20 contact trays and at high gas velocities, e.g. as described in British patent specification 1,362,384.

- In case H₂S was present in the original gas mixture the semi-lean solvent obtained in step c) contains H₂S and CO₂ in a high molar ratio. In view of the high content of H₂S this semi-lean solvent is not suitable to be used as solvent in step a) and the acid gases present therein have to be removed therefrom. The acid gases are removed from the said semi-lean solvent by total regeneration to yield lean solvent. The regeneration is very suitably carried out by heating in a regeneration column (e.g., to a temperature in the range of from 80 to 160°C), which heating is preferably carried out by stripping with steam.

The gas obtained during this regeneration has such an H₂S content that it can be suitably used in a Claus process for the preparation of sulphur.

- The lean solvent obtained after regeneration can very suitably be reused in step a), and also for contacting the flashed gas from step b) or c) if desired.

It will be clear that in order to keep the amount of energy needed in the process as low as possible, it is of advantage to carry out heat exchange of process streams where appropriate.

Example 1

- 10,000 kmol/h of a gas mixture (composition 80%v methane, 5%v ethane, 3%v propane, 1%v butane, 1%v H₂S and 10%v CO₂) are introduced into the bottom of an absorption column containing 30 valve trays, at a temperature of 40°C and a pressure of 50 bar. This gas mixture is countercurrently contacted with 300 m³/h of a lean solvent consisting of methyldiethanolamine (50%w), sulfolane (25%w) and water (25%w). Purified gas leaves the top of the absorption column in an amount of 9511.4 kmol/h; this gas contains 644 kmol/h CO₂ and less than 4 volume parts per million (ppm) of H₂S.

The loaded solvent (300 m³/h) is removed from the bottom of the absorption column; it contains 99.7 kmol/h H₂S and 356 kmol/h CO₂. This loaded solvent is flashed to a pressure of 15 bar at a temperature of 69.2°C. The gas flashed off (45 kmol/h) contains 1.4 kmol/h H₂S, 10.7 kmol/h CO₂, the balance consists of hydrocarbons. The loaded solvent obtained after this first flash contains 98.6 kmol/h H₂S and 345 kmol/h CO₂. This is heated by heat exchange with lean solvent

of 70°C. The gas set free during this second flash (293.6 kmol/h) consists of 35.6 kmol/h H₂S and 258 kmol/h CO₂. It is contacted countercurrently with 148 m³/h lean solvent in a second absorption column with 13 valve trays at a temperature of 40°C and a pressure of 1.1 bar, yielding 212 kmol/h of a gas which consists of CO₂ containing 300 ppm H₂S. The loaded solvent obtained in the last-mentioned absorption column is regenerated together with the semi-lean solvent obtained after the second flash. This semi-lean solvent contains 63 kmol/h H₂S and 87 kmol/h CO₂. The regeneration is carried out by stripping with steam, yielding a gas which consists of 98.6 kmol/h H₂S and 133 kmol/h CO₂, which gas is very suitable to be used in a Claus process. The lean solvent obtained after regeneration (448 m³/h) is partly (148 m³/h) recycled to the second absorption column and partly (300 m³/h) (after heat exchange with the loaded solvent from the first flash) used as lean solvent in the absorption column.

Example 2

10,000 kmol/h of a gas mixture (composition 90.65% methane and 9.35%v CO₂) are introduced into the bottom of an absorption column containing 20 valve trays at a temperature of 35°C and a pressure of 91 bar. This gas mixture is countercurrently contacted with 844 m³/h of a solvent which consists of methyldiethanolamine (50%w), sulfolane (25%w) and water (25%w). This solvent is semi-lean solvent; it contains 1374 kmol/h CO₂ and no methane. The gas leaving the top of the absorption column (9069 kmol/h) consists for 98% of methane, the balance being CO₂.

The loaded solvent (844 m³/h) is removed from the bottom of the absorption column; it contains 2131 kmol/h CO₂ and 174 kmol/h methane and has a temperature of 53°C. This loaded solvent is flashed to a pressure of 24 bar and a temperature of 51°C.

The gas flashed off (204 kmol/h) consists of 159 kmol/h methane and 45 kmol/h CO₂. The loaded solvent obtained after this first flash (844 m³/h) contains 2086 kmol/h CO₂ and 15 kmol/h methane. It is heated and flashed to a pressure of 1.3 bar and a temperature of 40°C. The gas set free during this second flash (727 kmol/h) consists of 15 kmol/h methane and 712 kmol/h CO₂. The semi-lean solvent obtained in the second flash (844 m³/h) contains 1374 kmol/h CO₂ and no methane, and is introduced at the top of the absorption column as solvent for the gas mixture to be purified as described above.

Comparative experiment

For comparison the same process as described in Example 2 is carried out with a solvent consisting of diisopropanolamine (50%w), sulfolane (25%w) and water (25%w) (not according to the invention). For the removal of the same amount of CO₂ from the feed gas, and the use of non-regenerated semi-lean solvent in the absorption step, a solvent circulation about five times as high as that needed in the process according to the invention described in Example 2 is needed. Moreover, about five times as much methane is absorbed per hour in the absorp-

amount of methane set free in this first flash is so high that for economical reasons this gas has to be recompressed and recycled, which makes the installation of expensive compressors necessary.

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CLAIMS

1. A process for removal of CO₂ and, if present, H₂S from a gas mixture, characterized in that:
 - a) the gas mixture is contacted at elevated pressure countercurrently with a solvent which comprises a tertiary amine and a physical absorbent;
 - b) the loaded solvent obtained is flashed at least once by pressure release to a pressure which is above the total partial pressure of the CO₂ and H₂S present in the loaded solvent at the prevailing temperature;
 - c) the loaded solvent obtained in step b) is flashed at least once by pressure release to a pressure which is below the total partial pressure of the CO₂ and H₂S present in the loaded solvent at the prevailing temperature, and semi-lean solvent obtained in step c) is, optionally after all or part thereof has been totally regenerated, used as solvent in step a).
2. A process according to claim 1, characterized in that the solvent contains water.
3. A process according to claim 1 or 2, characterized in that the tertiary amine is aliphatic and contains at least one hydroxyalkyl group per molecule.
4. A process according to claim 3, characterized in that the tertiary amine is methyldiethanolamine.
5. A process according to any one of the preceding claims, characterized in that the physical absorbent is tetrahydrothiophene 1,1-dioxide.
6. A process according to any one of the preceding claims, characterized in that the solvent contains methyldiethanolamine, tetrahydrothiophene 1,1-dioxide and water.
7. A process according to claim 6, characterized in that the solvent contains in the range of from 10 to 60% of methyldiethanolamine, in the range of from 15 to 55%w of tetrahydrothiophene 1,1-dioxide and in the range of from 5 to 35%w of water.
8. A process according to any one of the preceding claims, characterized in that in step a) the gas mixture is contacted with the solvent in a contacting zone which comprises in the range of from 15 to 80 contacting layers.
9. A process according to any one of the preceding claims, characterized in that step a) is carried out at a pressure in the range of from 20 to 100 bar.
10. A process according to any one of the preceding claims, characterized in that step a) is carried out at a contacting temperature in the range of from 20 to 80°C.
11. A process according to any one of the preceding claims, characterized in that the loaded solvent in step c) is flashed to atmospheric pressure.
12. A process according to any one of the preceding claims, characterized in that semi-lean solvent obtained in step c) is regenerated by strip-

a).

13. A process according to any one of claims 1-11, characterized in that the gas mixture is substantially free of H_2S and the semi-lean solvent obtained in step c) is used as the only solvent in step a).

14. A process as claimed in claim 1, substantially as hereinbefore described with reference to the Examples 1 and 2.

10 15. Gas mixtures from which CO_2 and, if present, H_2S have been removed by means of a process as claimed in any one of the preceding claims.

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